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A new processable and fluorescent polydithienylpyrrole electrochrome with pyrene appendages

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ABSTRACT

A new hybrid compound, namely 1-(pyren-3-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-P), was polymerized via both chemical and electrochemical methods. Chemically obtained soluble polydithienylpyrrole (c-PSNS-P) bearing pyrene appendages is a homogeneous and uniform polymer with a number averaged molecular weight of 15,200 g/mol. The polymer exhibits both multi-electrochromic and fluorescent properties. Upon oxidation, the color of electrochemically obtained polymer (e-PSNS-P) changes from yellowish orange to greenish yellow and to green/blue and finally to blue. In addition, the polymer induces yellowish orange (564 nm) and bright orange emission (613 nm) in solution and solid states, respectively.

1. Introduction

Functional conjugated polymers have attracted considerable attention since they are promising candidates to be amenable for use in a variety of advanced technological applications such as sensors [1–3], light emitting diodes [4,5], photovoltaic cells [6–8], transistors [9,10], electrochromic devices [11–13], and optical displays [14]. Especially, they have been thought as one of the most useful electrochromic materials due to their multicolors with the same material with a short response time under external applied low potentials. Also, they exhibit high optical contrast ratio between various redox states, high redox stability and long cycle life under ambient conditions as well as processing onto large area surfaces by spin and spray coatings [15] or roll-to-roll technique [16]. More importantly, all of these properties can be tuned by structural design of the starting material [17–19].

Recently, significant effort has been devoted to design and synthesize of novel, simple and effective functional and solution-processable polymeric materials [17–23]. Among these materials, dithienylpyrrole (SNS) is one of the most useful core units in order to obtain materials with distinct properties [19,24–35]. For instance, the flavin functionalized polydithienylpyrrole (PSNS) fabricated by electrochemical methods could be used for the detection of 2,6-diamidopyridine, which is a biologically important redox-active molecule [31]. Furthermore, it was recently shown that a chemiluminescent PSNS functionalized with luminol appendages could be used for the detection of reactive oxygen species [32]. In addition, by the help of fluorescent substituents like naphthalene and fluorene, PSNS based polymers could exhibit both fluorescent and electrochromic properties [13,36,37]. It was also shown that the intrinsic properties could easily be controlled through rational design of the backbone structures. Nonetheless, examples of processable fluorescent and electrochromic polymeric materials based on SNS unit have still been rare and newer ones are welcome. Moreover, SNS based materials can still be amplified to create viable materials.

In this context, pyrene can also be a good candidate for the functional SNS core since pyrene and its derivatives are valuable fluorescent probes, which can be used in sensors [38–42], LEDs [43,44], electrochromic [45], and transistors [46]. In spite of these numerous applications of pyrene and derivatives, only a few random copolymers of pyrene [47–50], have been reported, however, regioregular polymeric systems with pyrene scaffold are uncommon [51].

Herein we wish to report the fluorescent and electrochromic properties of a new processable polymer (PSNS-P), which is based on SNS with a pyrene appandage; namely, 1-(pyren-3-yl)-2,5-di(thiophen-2-yl)-1H-pyrrole (SNS-P). In this unique combination, SNS unit provides low oxidation potential as well as electrochromic features whereas pyrene appendage contributes with its fluorescence to this dual electrochromic and luminescent system. More

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importantly, the polymer, PSNS-P, had a specific optical band gap (2.27 eV) to reflect and/or transmit the yellowish orange color in the neutral state, and it could be switched to military green and blue colors upon oxidation. Note that these colors are essential for full color electrochromic device and display applications.

2. Experimental

All chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. 0.1 M $LiClO_4$ solution, dissolved separately in acetonitrile (ACN) and ethanol (EtOH), was used as electrolyte solutions. A platinum disk (0.02 cm^2) and a platinum wire were used as working and counter electrodes, respectively, as well as a Ag/AgCl reference and a Ag wire pseudoreference electrodes (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple which is an internal standard calibrated to be 0.44 V in ACN solution vs. Ag/AgCl, 0.44 V in ACN solution vs. Ag wire and 0.44 V in EtOH solution vs. Ag wire). Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Electro-optical properties were investigated by using an indium tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7 cm × 5 cm) electrode as well as a platinum wire as counter electrode and a Ag wire as a pseudoreference electrode. For the spectroelectrochemical measurements, the polymer film was coated on ITO electrode via cyclic voltammetry or constant potential electrolysis in 0.1 M $LiClO_4$/EtOH. In order to break in the polymer film, it was switched between 0.0 and 0.90 V in a monomer-free electrolytic solution. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat–galvanostat. The electro-optical spectra were monitored on a Specord S 600 spectrometer (standard illuminator D65, field of width 5° observer) and color space was given by the International Commission of Illumination with luminance (L^*), hue (a^*), and intensity (b^*). Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430 are the references of colorimetric measurements. FTIR spectra were recorded on Nicolet 510 FTIR with an attenuated total reflectance (ATR). GPC analysis of the polymer was carried out with Polymer Laboratories PL-GPC 220 instrument. Thermal gravimetric analysis was done via PerkinElmer Pyris 1 TGA under nitrogen atmosphere with 10 °C/min heating rate. The synthesis of **2**, **3** [52] and **4** [53] were carried out according to published procedures.

2.1. Synthesis of SNS-P (5)

A solution of 100 mg (0.4 mmol) 1,4-di(thiophen-2-yl)butane-1,4-dione (**4**), 90 mg (0.4 mmol) amino pyrene (**3**) and 3 mg p-toluenesulfonic acid in 50 mL dry toluene were heated under reflux in a Dean–Stark apparatus until all the starting materials were consumed. The flask was cooled and the solvent was removed under reduced pressure. The residue was filtered through a short pad of silica gel by eluting with CH_2Cl_2/hexane (1:1, v/v) to give analytically pure SNS-P (160 mg, 0.369 mmol) as brown solid in 92% yield. M.p. 239–240 °C; ^1H NMR (400 MHz, $CDCl_3$): δ/ppm: 8.22–8.18 (m, 2H), 8.15–8.10 (m, 3H), 8.02–7.95 (m, 3H), 7.56 (d, J = 10 Hz, 1H), 6.76 (s, 2H), 6.75 (dd, J = 5.0–1.0 Hz, 2H), 6.52 (dd, J = 5.0–3.6 Hz, 2H), 6.34 (dd, J = 3.6–1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm: 134.8, 132.1, 131.5, 131.1, 131.0, 130.8, 129.3, 128.6, 128.1, 127.3, 126.7, 126.5, 125.9, 125.1, 124.9, 124.4, 123.7, 123.6, 122.1, 109.8.

2.2. Chemical polymerization of SNS-P (5)

Compound SNS-P (80 mg, 0.186 mmol) was dissolved in chloroform (30 mL). A solution of anhydrous $FeCl_3$ (254.2 mg, 0.93 mmol) in nitromethane was added dropwise over a period of 45 min to the stirred monomer at room temperature (the bright yellow monomer solution turned progressively dark brown with addition of oxidizing agent). The mixture was stirred 48 h at room temperature. It was then precipitated into methanol (100 mL). The precipitate was filtered, redissolved in chloroform (100 mL), and stirred for 6 h with hydrazine monohydrate (4 mL) (the color of the solution was turned from dark brown to dark orange after addition of the hydrazine monohydrate). After evaporation, the concentrate was precipitated into methanol (100 mL), the precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 48 h with methanol. The polymer was extracted with chloroform and soluble and insoluble parts were obtained by 33% and 67% yields, respectively.

3. Results and discussion

Pyrene (**1**) was chosen as the starting material for the synthesis of SNS-P. Nitration of **1** with $Cu(NO_3)_2$ in the presence of acetic anhydride afforded nitropyrene **2**, which was reduced with hydrazine in the presence of Pd/C (10%) to give aminopyrene **3**. Paal–Knorr reaction of aminopyrene **3** with **4** in the presence of catalytic amount of PTSA in Dean–Stark trap provided the target compound in 92% yield. SNS-P initially characterized on the basis of ^1H, ^{13}C NMR and FTIR analysis, which firmly established the structure.

The electronic absorption and emission spectra of SNS-P, SNS [54] and pyrene were given in Fig. 1. The absorption spectrum of SNS unit consisted of two broad bands centered at around 230 nm and 330 nm (π–π^*). On the other hand, absorption spectrum of pyrene had six different sets of bands centered at 241 nm, 263 nm, 275 nm, 308 nm, 321 nm and 337 nm. However, the absorption spectrum of SNS-P contained all the absorption bands of each units (SNS and pyrene), as expected. It was noted that the emission of both SNS and pyrene were blue, whereas SNS-P emitted yellowish light.

The electrochemical behavior of the SNS-P was investigated in an electrolyte solution containing 0.1 M $TBAPF_6$ dissolved in ACN solution. As shown in Fig. 2, during anodic scan, the monomer exhibits a lower oxidation peak of 0.89 V vs. Ag/AgCl than its main components: pyrene (1.41 V vs. Ag/AgCl) and SNS (1.12 V vs. Ag/AgCl) units. It confirmed that a strong electronic interaction exists between the HOMO levels of the pyrene and the SNS units. This indicated that attempted oxidation of the monomer at this low potential would result in polymerization through SNS units without disturbing and the cleavage of the pyrene unit. Similar results were also observed in the cases of fluorene and naphthalene derived SNS monomers [37].

On that basis, the electropolymerization was performed via cyclic voltammetry technique between 0.0 V and 1.00 V, but interestingly the monomer did not give the corresponding polymer on the surface of the electrode in acetonitrile, ACN, solution. It was also the case when dichloromethane, DCM, was used as a solvent. Most probably, the product was quite soluble in these solvents and the electrodeposition did not take place at all. For that reason, the electropolymerization was carried out in 0.1 M $LiClO_4$ dissolved in EtOH, which had a suitable potential range (from 0.0 V to 1.0 V) for the polymerization (Fig. 3b). SNS-P monomer underwent polymerization easily during repetitive cycles between 0.0 V and 0.85 V vs. Ag wire. Fig. 3a shows a characteristic signature of the formation of an electroactive polymer film; after first cycle, a new redox couple started to appear and intensified after each cycle (Scheme 1).

Electrochemically obtained polymer film, e-PSNS-P, on ITO (Scheme 2) shows a reversible redox couple with a half wave of 0.44 V vs. Ag/AgCl (Fig. 4a) in a monomer free electrolyte solution containing 0.1 M $TBAPF_6$/ACN and this value was smaller than fluorene (0.54 V) and naphthalene (0.56–0.61 V) analogs [37]. The